

Data collection

Siemens P4 diffractometer $\theta_{\max} = 25^\circ$
 ω scans $h = 0 \rightarrow 26$
 Absorption correction: none $k = -9 \rightarrow 1$
 2603 measured reflections $l = -19 \rightarrow 16$
 2273 independent reflections 3 standard reflections
 2074 reflections with every 97 reflections
 $I > 2\sigma(I)$ intensity decay: none
 $R_{\text{int}} = 0.015$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.068$
 $S = 1.052$
 2273 reflections
 311 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 0.6765P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.14 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.12 \text{ e } \text{\AA}^{-3}$

Extinction correction:
SHELXL97 (Sheldrick, 1997)
 Extinction coefficient:
 0.0052 (4)
 Scattering factors from
International Tables for Crystallography (Vol. C)
 Absolute structure: Flack (1983)
 Flack parameter: not reliably determined

Table 1. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H1WA...N12	0.94 (3)	1.97 (3)	2.906 (3)	175 (3)
O1W—H1WB...O3W ^a	0.78 (3)	1.96 (3)	2.736 (3)	176 (3)
O2W—H2WA...N11	0.76 (3)	2.12 (3)	2.883 (3)	175 (3)
O2W—H2WB...O1W ⁱⁱ	0.80 (3)	1.99 (3)	2.788 (3)	176 (3)
O3W—H3WA...N32	0.83 (3)	2.07 (3)	2.885 (3)	170 (3)
O3W—H3WB...O5W ⁱⁱⁱ	0.88 (3)	1.83 (3)	2.711 (3)	176 (3)
O4W—H4WA...N21	0.87 (3)	2.05 (3)	2.928 (3)	178 (3)
O4W—H4WB...O2W ^{iv}	0.80 (3)	2.01 (3)	2.812 (3)	173 (3)
O5W—H5WA...N31	0.82 (3)	2.11 (4)	2.928 (3)	174 (3)
O5W—H5WB...O4W ^a	0.80 (3)	1.97 (4)	2.771 (3)	172 (3)

Symmetry codes: (i) $x, y - 1, z$; (ii) $x - \frac{1}{2}, -\frac{1}{2} - y, z - \frac{1}{2}$; (iii) $x, 1 + y, z$; (iv) $x, -y, \frac{1}{2} + z$.

All non-H atoms were refined with anisotropic atomic displacement parameters. H atoms bonded to C atoms were placed at calculated positions, with isotropic displacement parameters riding on U_{eq} of the carrier atoms. H atoms bonded to O atoms were located from difference maps and refined with a common fixed atomic displacement parameter of 0.04 \AA^2 .

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Sheldrick, 1990a). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1339). Services for accessing these data are described at the back of the journal.

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C—H...O interactions in dimethyl 6,6'-dimethoxy-3,3',5,5'-tetramethylbiphenyl-2,2'-dicarboxylate

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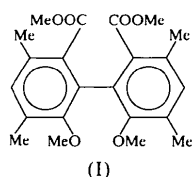
Abstract

The title compound, C₂₂H₂₆O₆, crystallized in the centrosymmetric space group *Pbcn* with half of the molecule as the asymmetric unit (the molecular symmetry is 2). The H atoms of each of the four methyl groups in the asymmetric unit are disordered over two sites. Nine leading C—H...O interactions are present, with H...O distances ranging from 2.50 to 2.87 \AA and C...O distances ranging from 3.157 (3) to 3.567 (3) \AA . The various interaction chains form a three-dimensional network. The intramolecular angle between the biphenyl ring planes (twist angle) is $71.3 (1)^\circ$.

Comment

This report is one of a series on hydrogen-bonding and C—H...O interactions in aromatic compounds, and follows reports on other substituted biphenyls including, for example, biphenyl-3-carboxylic acid, 6,6'-dimethylbiphenyl-2,2'-dicarboxylic acid and 6,6'-dimethoxy-3,3',5,5'-tetramethylbiphenyl-2,2'-dimethanol (hereafter,

DTBD) (Blackburn *et al.*, 1996; Gerkin, 1998; Dobson & Gerkin, 1999). In the title ester, (I), substantial C—H...O interaction is expected since there are no conventional hydrogen-bond donors and six potential acceptors, *i.e.* atoms O1–O6.



Ester (I) crystallized in the centrosymmetric space group *Pbcn* with half the molecule as the asymmetric unit (the molecular symmetry is 2) and with the H atoms of each methyl group disordered over two sets of sites. The refined asymmetric unit and the numbering scheme are given in Fig. 1. The refined occupancies of the H-atom sites, arbitrarily named *A* and *B*, at the C8, C9, C10 and C11 methyl groups are, respectively, 0.48 (3) and 0.52, 0.79 (2) and 0.21, 0.65 (2) and 0.35, and 0.59 (3) and 0.41. As expected, a number of C—H...O interactions occur with parameters falling well within the limits suggested by Taylor & Kennard (1982) for significant interactions; geometrical details for the nine leading interactions are given in Table 2. Realistic analysis of these interactions requires departure from standard graph-set analysis (Bernstein *et al.*, 1995), as we now delineate. Since all of the C—H donors occur in methyl groups with their H atoms disordered randomly over two sets of sites (designated arbitrarily as *A* and *B* at each methyl C atom), if, in the usual manner, each unique C—H...O interaction were to be used for graph-set analysis, chain patterns would not be generated. As a specific example, we consider the first-level graph for the first-listed interaction in Table 2; in the absence of disorder, we would find the descriptor *C*(8), but, with disorder, after one occurrence of C8—H8A2...O3ⁱ [symmetry code: (i) $1-x, 1+y, \frac{1}{2}-z$], the methyl H atoms at C8ⁱ might well be in the *B* configuration and propagation of the *A* chain would be impossible. Clearly, what would be chain patterns in the ordered case would become finite patterns comprising 1, 2, 3,.... 'chained' occurrences of the given interaction before its interruption by disorder. In the present case, since at least one significant *A* and one significant *B* interaction link a given C-atom donor to a given O-atom acceptor, the physical situation (which includes chains) will be properly accounted for if these interactions (normally treated as distinct) are regarded as equivalent (interchangeable). Then, as shown in Table 2, four such groups of interactions are present. For graph-set analysis, these are designated α – δ in their order of appearance in Table 2. The results of the modified analysis for the basic first- and second-level graph sets are given in Table 3. The chains propagate variously

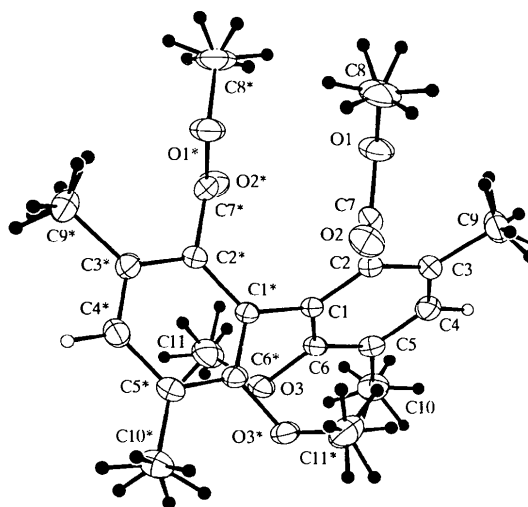


Fig. 1. ORTEP (Johnson, 1976) drawing of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn for 20% probability for all non-H atoms, while open spheres of arbitrary small radius depict H atoms. H atoms of fractional occupancy are represented by solid spheres. [Symmetry code: (*) $1-x, y, \frac{1}{2}-z$].

along [010], [001], [100] and $[1\bar{1}0]$ to form a three-dimensional network of interactions.

The phenyl ring of the asymmetric unit is nearly planar, the maximum deviation of any of its atoms from the best-fit plane describing them being 0.012 (2) Å, while the average deviation is 0.008 (4) Å. The dihedral angle between the two rings comprising the biphenyl core, the biphenyl twist angle, is 71.3 (1)°. The torsion angle C2—C1—C1*—C2* is 74.1 (4)°, while C2—C1—C1*—C6* is -108.5 (1)°. For geometric comparisons of the biphenyl core of (I), the DTBD molecule, cited above, serves well since it is very similarly substituted; for DTBD, the maximum deviations of any of its ring atoms from the best-fit planes describing them are 0.011 (2) and 0.014 (2) Å, while the biphenyl twist angle is 87.3 (1)°. In (I), the non-H atoms of the ester group (O1, O2, C7 and C8) lie very nearly in a plane, their maximum deviation from the best-fit plane describing them being 0.005 (2) Å. The dihedral angle between the best-fit planes of the phenyl ring and the ester group is 62.2 (1)°. The spatial relations among the various parts of (I) are illustrated in the packing diagram (Fig. 2).

Selected bond distances and angles of (I) are given in Table 1. All distances and angles fall within normal limits. The closest intermolecular approaches, excluding pairs of atoms involved in the tabulated C—H...O interactions, are between H9B1 and H11A3^v [symmetry code: (v) $1-x, 1-y, 1-z$] and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.28 Å. This result suggests that there is a somewhat enhanced probability for the H atoms on C11 to be of the same site-type as the H atoms on C9; in that case, the closest intermolecular approach is then between C8

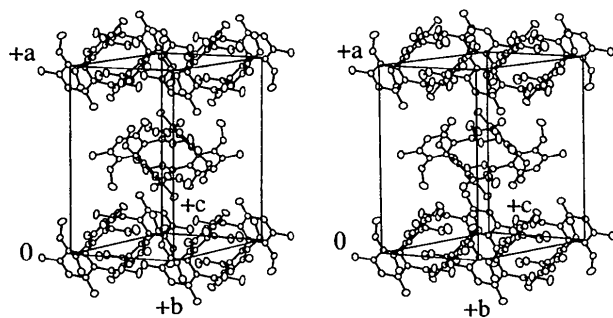


Fig. 2. ORTEPII (Johnson, 1976) packing diagram of (I). Displacement ellipsoids are drawn for 20% probability for all non-H atoms and all H atoms have been omitted for clarity.

and H11A1ⁱ, and is 0.02 Å less than the corresponding Bondi sum.

Compound (I) was among a series of highly hindered biphenyls chosen for an electrochemical investigation of heterogeneous electron transfer by Grzeszczuk & Smith (1986).

Experimental

Compound (I) was obtained from the chemical collection of Dr M. S. Newman as clear colorless crystals. One of these was chosen as the experimental sample. A synthesis of (I) has been described by Newman & Dali (1977).

Crystal data

C₂₂H₂₆O₆
M_r = 386.44
 Orthorhombic
Pbcn
a = 14.898 (1) Å
b = 9.190 (2) Å
c = 15.525 (2) Å
V = 2125.6 (8) Å³
Z = 4
D_x = 1.207 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 11.3–14.2°
 μ = 0.087 mm⁻¹
T = 296 K
 Prism
 0.35 × 0.31 × 0.31 mm
 Colorless

Data collection

Rigaku AFC-5S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 2455 measured reflections
 2455 independent reflections
 1069 reflections with $I > 2\sigma(I)$

θ_{\max} = 27.56°
 $h = 0 \rightarrow 19$
 $k = 0 \rightarrow 11$
 $l = -20 \rightarrow 0$
 6 standard reflections
 every 150 reflections
 intensity decay: 3.58%

Refinement

Refinement on *F*²
R(*F*) = 0.055
wR(*F*²) = 0.074
S = 1.35
 2454 reflections
 132 parameters

$\Delta\rho_{\max}$ = 0.40 e Å⁻³
 $\Delta\rho_{\min}$ = -0.39 e Å⁻³
 Extinction correction:
 Zachariasen (1963, 1968)
 Extinction coefficient:
 4.3 (3) × 10⁻⁷

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2_{cs} + (0.005I)^2]$
 $(\Delta/\sigma)_{\max} = 0.0002$

Scattering factors from Stewart *et al.* (1965) (H) and Creagh & McAuley (1992) (C, O)

Table 1. Selected geometric parameters (Å, °)

O1—C7	1.338 (3)	O3—C6	1.380 (2)
O1—C8	1.445 (3)	O3—C11	1.406 (3)
O2—C7	1.197 (3)	C1—C1*	1.497 (4)
C7—O1—C8	116.6 (2)	O1—C7—C2	110.6 (2)
C6—O3—C11	115.6 (2)	O2—C7—C2	125.6 (2)
O1—C7—O2	123.8 (2)		

Symmetry code: (*) 1 - *x*, *y*, $\frac{1}{2} - z$.

Table 2. Leading C—H...O interactions (Å, °)

No s.u.'s are given for quantities involving H atoms since they are fixed.

D—H...A	D—H	H...A	D...A	D—H...A
α set				
C8—H8A2...O3 ⁱ	0.98	2.50	3.157 (3)	124
C8—H8B1...O3 ⁱ	0.98	2.73	3.157 (3)	107
C8—H8B2...O3 ⁱ	0.98	2.78	3.157 (3)	104
β set				
C10—H10A1...O2 ⁱⁱ	0.98	2.75	3.567 (3)	141
C10—H10B3...O2 ⁱⁱ	0.98	2.77	3.567 (3)	139
γ set				
C11—H11A1...O2 ⁱⁱⁱ	0.98	2.63	3.382 (3)	134
C11—H11B1...O2 ⁱⁱⁱ	0.98	2.87	3.382 (3)	113
δ set				
C11—H11A2...O2 ^{iv}	0.98	2.81	3.510 (3)	129
C11—H11B3...O2 ^{iv}	0.98	2.73	3.510 (3)	137

Symmetry codes: (i) 1 - *x*, 1 + *y*, $\frac{1}{2} - z$; (ii) *x*, 1 - *y*, $\frac{1}{2} + z$; (iii) $\frac{1}{2} + x$, *y* - $\frac{1}{2}$, $\frac{1}{2} - z$; (iv) 1 - *x*, *y*, $\frac{1}{2} - z$.

Table 3. Basic first- and second-level graph-set descriptors involving C—H...O interactions which are designated by donor-acceptor group sets α – δ in the order given in Table 2

α	β	γ	δ
C(8)	<i>R</i> ₁ ¹ (20)	<i>C</i> ₂ ² (8)	<i>C</i> ₂ ² (8) <i>S</i> (9)
β	C(8)	<i>C</i> ₂ ² (8)	<i>R</i> ₂ ² (16) <i>S</i> (9)
γ		C(8)	<i>C</i> ₂ ² (4) <i>S</i> (9)
δ			<i>S</i> (9)

Data collection: *MSCI/AF C Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCI/AF C Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1207). Services for accessing these data are described at the back of the journal.

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Hydrogen bonding and C—H···X interactions in two triclinic phases of 4-carboxyquinolinium chloride monohydrate

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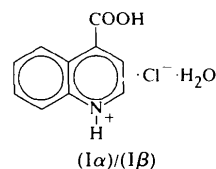
Abstract

The title substance, $C_{10}H_8NO_2^+ \cdot Cl^- \cdot H_2O$, crystallized in the centrosymmetric space group $P\bar{1}$ in two phases, α and β , each with one organic cation, one Cl^- ion and one water molecule in the asymmetric unit. The principal structural difference in the two asymmetric units lies in the relative orientation of the water molecule. Three hydrogen bonds in the α phase have donor–acceptor distances (N···Cl or O···Cl) ranging from 3.052 (1) to 3.189 (2) Å, while one has an O···O distance of 2.603 (3) Å. Three hydrogen bonds in the β

phase have donor–acceptor distances (N···Cl or O···Cl) ranging from 3.044 (2) to 3.206 (2) Å, while two have O···O distances of 2.586 (2) and 3.147 (3) Å. The H atoms in all these hydrogen bonds are ordered. Each of these phases has five leading C—H···X interactions, for which the H···X distances are less than, or at most slightly greater than, the corresponding van der Waals radius sums. Taken together, these hydrogen bonds and C—H···X interactions form a three-dimensional network of interactions in each phase. The dihedral angle between the best-fit quinoline core plane and the carboxyl group plane is 25.9 (1)° for the α phase and 20.0 (1)° for the β phase.

Comment

Early compositional and crystallographic studies of solids obtained from aqueous solutions containing quinoline-4-carboxylic acid characterized a number of phases (Weidel, 1874; Claus & Kickelhayn, 1887; Muthmann & Nef, 1887; Muthmann, 1889; Skraup, 1880; Stuhlmann, 1888); these solids included both anhydrous and hydrated phases. We have previously reported structures of a monoclinic anhydrous phase (Dobson & Gerkin, 1998), a monoclinic dihydrate (Dobson & Gerkin, 1999a), and a triclinic trihydrate (Dobson & Gerkin, 1999b). Following addition of HCl to the parent solutions in attempts to crystallize the triclinic dihydrate phase of quinoline-4-carboxylic acid, two previously undescribed phases, ($I\alpha$) and ($I\beta$), were obtained and are characterized in this report.



The two phases of the title compound, ($I\alpha$) and ($I\beta$), crystallized in the centrosymmetric triclinic space group $P\bar{1}$, with one organic cation, one Cl^- ion and one water molecule in each of the asymmetric units. The refined asymmetric units and the atom-numbering schemes are shown in Fig. 1.

Four strong conventional hydrogen bonds are formed in the α phase, while four strong bonds and one weaker bond are formed in the β phase. The H atoms in all these hydrogen bonds are ordered. Geometric details of these bonds are given in Tables 2 and 5. The rather modest differences in the two sets of strong conventional hydrogen bonds, as well as the presence of the fifth weaker one in the β phase, arise principally from the somewhat different relative orientation of the water molecule in the two asymmetric units.